

Charge transfer model for the electronic structure of layered ruthenates

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Motivated by the earlier experimental results and *ab initio* studies on the electronic structure of layered ruthenates (Sr_2RuO_4 and Ca_2RuO_4) we introduce and investigate the multiband $d-p$ charge transfer model describing a single RuO_4 layer, similar to the charge transfer model for a single CuO_2 plane including apical oxygen orbitals in high T_c cuprates. The present model takes into account nearest-neighbor anisotropic ruthenium-oxygen $d-p$ and oxygen-oxygen $p-p$ hopping elements, crystal-field splittings and spin-orbit coupling. The intraorbital Coulomb repulsion and Hund's exchange are defined not only at ruthenium but also at oxygen ions. Our results demonstrate that the RuO_4 layer cannot be regarded to be a pure ruthenium t_{2g} system. We examine a different scenario in which ruthenium e_g orbitals are partly occupied and highlight the significance of oxygen orbitals. We point out that the predictions of an idealized model based on ionic configuration (with $n_0 = 4 + 4 \times 6 = 28$ electrons per RuO_4 unit) do not agree with the experimental facts for Sr_2RuO_4 which support our finding that the electron number in the $d-p$ states is significantly smaller. In fact, we find the electron occupation of d and p orbitals for a single RuO_4 unit $n = 28 - x$, being smaller by at least 1–1.5 electrons from that in the ionic model and corresponding to self-doping with $x \simeq 1.5$.

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I. INTRODUCTION

The description of the electronic states of transition metal oxides with partly filled d orbitals is not an easy task, and one usually looks for some simplifications. Models for manganites are complex as they involve partly filled t_{2g} and e_g orbitals [1]. Systems with partly filled t_{2g} orbitals and empty e_g orbitals, such as for titanates [2] or vanadates [3] or with completely filled t_{2g} and partly filled e_g orbitals as in cuprates [4] or nickelates [5] are much easier to investigate. Such systems can be realized if the gap separating t_{2g} from e_g orbital states (induced by crystal-field effects) is sufficiently large.

The transition-metal oxides with $4d$ ions are even more challenging as there electron correlations are somewhat weaker and simultaneously spin-orbit coupling plays an important role. Therefore one has to treat $4d$ electrons as both itinerant and strongly correlated, in the vicinity of a metal-insulator transition. The compound which belongs to this class and received a lot of attention is Sr_2RuO_4 as it became a candidate for a p -wave superconductor [6]. Recent progress in photoemission technique made it possible to investigate the many-body effects both in bulk and surface bands of Sr_2RuO_4 [7]. Spin-orbital entangled states have been seen recently in spin- and angle-resolved photoemission spectroscopy [8]. Such states arise in correlated transition metal oxides either on superexchange bonds [9] or locally due to strong spin-orbit coupling at transition-metal sites [10]. Indeed, these quantum effects play an important role in Mott insulators with $4d$ ions [11] and in these systems doped by $3d$ elements [12, 13].

In Sr_2RuO_4 the experiments support the earlier implementation of spin-orbit coupling within the local den-

sity approximation with Coulomb interaction U treated in LDA+ U approach which show that both Coulomb U and the spin-orbit coupling are necessary for a correct description of the Fermi surface in Sr_2RuO_4 [14]. The electronic structure of Sr_2RuO_4 was extensively studied in the past [15] and it was established that the orbital physics plays here an important role [16]. In Ca_2RuO_4 the bandwidth is smaller but the effects of spin-orbit coupling are even more pronounced [17].

Due to a rather large crystal-field splitting between t_{2g} to e_g levels ~ 3.5 eV in Ca_2RuO_4 and Sr_2RuO_4 [18], one might expect that these compounds are also purely t_{2g} systems. This picture was also supported by the earlier studies of electronic structure in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ by photoemission [19]. Orbital polarization is then helpful to understand the x-ray absorption measurements and is of importance in describing the insulating state of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [20]. A unique feature of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ is that slight changes in lattice parameters can induce drastic modifications of the character of their electronic ground states — Sr_2RuO_4 is metallic and superconducting at low temperature [6], whereas Ca_2RuO_4 is distorted and undergoes a metal-insulator transition [21]. Interest in these materials is also motivated by very unusual invar effect reported recently [22] which suggests spin-orbital entanglement [9] in the ground state.

Recently a simple tight-binding model was employed to investigate the superconductivity in Sr_2RuO_4 [23]. The simplest $d-p$ model would just include three t_{2g} orbitals per Ru and three $2p$ orbitals per O ion. However, there are serious doubts about the validity of this simplified physical picture. First, there are *ab initio* cluster+embedding computations by Kaplan and Soullard [24] who claim that the p -orbital charges on oxygens (in

Sr_2RuO_4) are not close to formal 6.0 as they follow from the ionic model, but are instead close to 5.0, and that in addition e_g levels are partly occupied. At the same time the transfer of charge from any strontium ion (to ruthenium-oxygen layer) is smaller than a formal value of 2 electrons. Secondly, a similar system, namely CoO_2 layer was also believed to be pure t_{2g} systems. However, it was shown [25] that e_g orbitals (in a doped system) can become very important, even in the absence of spin-orbit coupling. We show below that the total electron density which follows from the idealized ionic model with formal electronic charges does not describe correctly the electronic structure of Sr_2RuO_4 . In contrast, the $d-p$ model with reduced electron density based on *ab initio* calculations [24] gives results which agree with experiment.

To resolve the question about actual electron density within e_g orbitals in Sr_2RuO_4 we constructed a multiband charge-transfer model and performed unrestricted Hartree-Fock computations on a finite RuO_4 cluster which contains 4×4 Ru ions and $4 \times 4 \times 4$ oxygen ions — half of them located within the same plane as Ru ions, while the second half belonging to the elongated RuO_6 octahedra and surrounding the plane from above and below, being in out-of-plane (apical) positions. We imposed cyclic boundary conditions. The model involves (per a single RuO_4 unit) five $4d$ orbitals on Ru and 4×3 oxygen $2p$ orbitals per unit cell occupied by: (i) $n_0 = 4 + 4 \times 6$ electrons, according to the formal and idealized ionic model; (ii) the electron number lower by at least one electron, i.e., $n = 3 + 4 \times 6$ electrons or even smaller (we study below the case of $n = 2.5 + 4 \times 6$ electrons), as found in Ref. [24].

The paper is organized as follows. In Sec. II we introduce the multiband model which includes all $4d$ states at ruthenium ions and $2p$ states at oxygen ions. The parameters of the model are specified in Sec. III. The Hartree-Fock approximation for the Coulomb interactions is explained in Sec. IV, while in Sec. V we present the results of numerical calculations and we introduce the concept of self-doping with respect to the electron densities in the ionic model. The paper is concluded with a short discussion and summary of the main results in Sec. VI. In the Appendix we give the hopping elements $d-p$ and $p-p$, respectively.

II. MODEL HAMILTONIAN

In this section we introduce the $d-p$ charge-transfer Hamiltonian for RuO_4 plane (such as realized in Sr_2RuO_4). It consists of several parts,

$$\mathcal{H} = H_{\text{kin}} + H_{\text{so}} + H_{\text{diag}} + H_{\text{int}}. \quad (2.1)$$

The different terms in Eq. (2.1) stand for the kinetic energy (H_{kin}), spin-orbit coupling (H_{so}), crystal-field splittings which are diagonal in the $\{4d, 2p\}$ orbital basis

(H_{diag}), and the intraatomic Coulomb interactions (H_{int}) — they all are explained below.

A. Kinetic energy in hybridized $d-p$ bands

The kinetic part of the Hamiltonian is:

$$H_{\text{kin}} = \sum_{\{i,\mu;j,\nu\},\sigma} \left(t_{i,\mu;j,\nu} c_{i,\mu,\sigma}^\dagger c_{j,\nu,\sigma} + H.c. \right), \quad (2.2)$$

where we employ a general notation, with $c_{j,\nu,\sigma}^\dagger$ standing for the creation of an electron at site j in an orbital ν with up and down spin, $\sigma = \uparrow, \downarrow$. The model includes all $4d$ orbital states per Ru atom, $\nu \in \{xy, yz, zx, x^2 - y^2, 3z^2 - r^2\}$, and three $2p$ orbitals per oxygen atom, $\nu \in \{p_x, p_y, p_z\}$. Alternatively, i.e., choosing a more intuitive notation, we can write $d_{j,\nu,\sigma}^\dagger$ for d orbitals, while $p_{j,\nu,\sigma}^\dagger$ for p orbitals.

The matrix $t_{i,\mu;j,\nu}$ is assumed to be non-zero only for nearest neighbor ruthenium-oxygen $d-p$ pairs, and for nearest neighbor oxygen-oxygen $p-p$ pairs. The next nearest hopping elements, in particular direct ruthenium-ruthenium ones, and those between the p orbitals of neighboring apical oxygens are neglected. The nonzero $t_{i,\mu;j,\nu}$ elements are listed in the Appendix.

B. Spin-orbit coupling in layered ruthenates

Formally, simplified spin-orbit part H_{so} of the Hamiltonian Eq. (2.1) has a similar mathematical structure to the kinetic part H_{kin} [26–30], with $t_{\mu,\sigma;\nu,\sigma'}^{so}$ elements restricted to single ruthenium sites,

$$H_{\text{so}} = \sum_i H_{\text{so}}^{(i)} = \sum_i \left\{ \sum_{\mu \neq \nu; \sigma, \sigma'} t_{\mu,\sigma;\nu,\sigma'}^{so} d_{i,\mu,\sigma}^\dagger d_{i,\nu,\sigma'} + H.c. \right\} \quad (2.3)$$

where the summation runs only over ruthenium sites and where we explicitly use $d_{i,\nu,\sigma'}^\dagger$ operators for the $4d$ orbitals at Ru sites. The derivation of spin-orbit coupling starts from a single-site model. Using the $\{|i, \mu, \sigma\rangle\}$ basis one evaluates the full matrix of scalar products, $\langle i, \nu, \sigma' | \mathbf{L}_i \cdot \mathbf{S}_i | i, \mu, \sigma \rangle$, of angular momentum \mathbf{L}_i with spin \mathbf{S}_i operator (at site i). The individual single-site terms in $H_{\text{so}}^{(i)}$ are defined by on-site hopping-like elements, $t_{i,\nu,\sigma';\mu,\sigma}^{so}$ (between different spin and orbital states), and one arrives at the matrix form in Eq. (2.3).

As we use here the basis of real $4d$ orbitals (and not the spherical harmonics) several spin-orbit elements turn out to be purely imaginary (hence the hermitian Hamiltonian is not real but complex). The elements of the matrix t^{so} for a ruthenium site i are the following ones (for a similar result consult Fig. 6 in Ref. [27]),

$$H_{\text{so}}^{(i)} = \frac{\zeta}{2} \begin{bmatrix} 0 & 0 & 0 & 2i & 0 & 0 & 1 & -i & 0 & 0 \\ 0 & 0 & i & 0 & 0 & -1 & 0 & 0 & i & -\sqrt{3}i \\ 0 & -i & 0 & 0 & 0 & i & 0 & 0 & -1 & \sqrt{3} \\ -2i & 0 & 0 & 0 & 0 & 0 & i & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{3}i & -\sqrt{3} & 0 & 0 \\ 0 & -1 & -i & 0 & 0 & 0 & 0 & 0 & -2i & 0 \\ 1 & 0 & 0 & -i & -\sqrt{3}i & 0 & 0 & -i & 0 & 0 \\ i & 0 & 0 & 1 & -\sqrt{3} & 0 & i & 0 & 0 & 0 \\ 0 & i & -1 & 0 & 0 & 2i & 0 & 0 & 0 & 0 \\ 0 & \sqrt{3}i & \sqrt{3} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \quad (2.4)$$

where ζ is the spin-orbit coupling parameter and where the columns and rows are labeled in the following order:

$$(xy \uparrow), (yz \uparrow), (zx \uparrow), (x^2 - y^2 \uparrow), (3z^2 - r^2 \uparrow), \\ (xy \downarrow), (yz \downarrow), (zx \downarrow), (x^2 - y^2 \downarrow), (3z^2 - r^2 \downarrow).$$

Note that the consequence of finite spin-orbit coupling ζ is nonconservation of the z th component of the total spin and therefore the obtained ground state wave function is not a product of two Slater determinants for \uparrow - and \downarrow -spin. In some cases the spin-orbit coupling H_{so} can be treated as a minor perturbation and can be neglected when the average value of local angular momentum (at site i) is quenched to zero due to suitably strong crystal-field effects and low enough local symmetry (reduced by nearest neighbor atoms). Then, the spin-orbit Hamiltonian can contribute to total energy only as second-order correction. Such a reasoning however allows one to make only qualitative predictions.

An explicit treatment of spin-orbit coupling causes some difficulties. It is likely that the true ground states are not homogeneous in space, e.g. involving spin spirals or other micro-modulations, thus they may be considered intractable within Hartree-Fock computations for $d-p$ clusters (they have too many order parameters to converge). One can only hope that these micro-modulations are of secondary importance. We assume this scenario and to have a tractable model we decided to use a simplified approach. Namely, we break the symmetry along natural quantization axis which is the z -th axis (perpendicular to RuO_4 layer). We emphasize that the averages of local spin components aligned parallel to the (a, b) plane are assumed to be zero. To present this assumption in a more transparent way we can write down the formula for a local spin-flip, $S_{i,\mu}^+ = d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow}$, and a similar one for $S_{i,\mu}^-$. Thus the requirements that $\langle S_{i,\mu}^+ \rangle = \langle S_{i,\mu}^- \rangle = 0$ are equivalent to setting to zero the following order parameters with opposite spins, $\langle d_{i,\mu,\sigma}^\dagger d_{i,\mu,-\sigma} \rangle = 0$.

In Sec. V we report a study of charge space-homogeneous solutions. All occupation numbers, i.e., primary order parameters, are assumed to be the same for equivalent ruthenium ions and similar for oxygen ions. When studying the possibility of antiferromagnetism there are two sublattices — thus the number of order parameters doubles. Looking for charge space-

homogeneous ground states can be considered a simplification but from another point of view it can be treated as a consequence of strong long-range interionic electrostatic interactions. These interactions are not explicitly included in the model (2.1) at present. We remark that long-range interionic interactions cannot be easily incorporated into a typical $d-p$ model but instead they can be accounted for by requiring that individual ionic charges are space-homogeneous in accordance with crystal symmetry.

C. Crystal-field splittings

Let us now return to the $d-p$ Hamiltonian (2.1). The next part of the model H_{diag} is diagonal in the orbital basis and depends only on electron number operators. It takes into account the effects of crystal field and the difference of reference orbital energies (here we employ the electron notation),

$$\Delta = \varepsilon_d - \varepsilon_p, \quad (2.5)$$

between d and p orbitals, both for empty states without the Hartree terms which follow from H_{int} . Below we fix the reference energy ε_d for d orbitals to zero, hence we use only ε_p as a parameter and write:

$$H_{\text{diag}} = \sum_{i,\mu=x,y,z;\sigma} \varepsilon_p p_{i,\mu,\sigma}^\dagger p_{i,\mu,\sigma} + \sum_{i,\mu=x,y,z,\dots;\sigma} f_{\mu,\sigma}^{cr} d_{i,\mu,\sigma}^\dagger d_{i,\mu,\sigma}. \quad (2.6)$$

Here the first sum is restricted to oxygen sites, while the second one runs over ruthenium sites.

What concerns the value of ε_p , it could be different for in-plane and for out-of-plane (apical) oxygens. According to the earlier studies [31, 32] this difference can be as large as 1.5 eV. But such a large value follows from a simplified procedure of fitting electronic bands to the LDA results. In the framework of the present $d-p$ model one should expect much smaller difference, if any. The zero difference was assumed in computations performed in Ref. [33] and we also adopt this value. Here we remark that our test Hartree-Fock computations performed using a big 1.5 eV splitting give large differences in charge

occupation between in-plane and apical oxygens, in disagreement with the results of the population analysis in Ref. [24]. This choice is indeed unrealistic as in addition one obtains only ferromagnetic ground states, see below.

Let us return again to H_{diag} . The vector containing the elements of $\{f_{\mu,\sigma}^{cr}\}$ can be expressed as

$$f^{cr} = \frac{1}{3} D_1 \begin{bmatrix} 2 \\ -1 \\ -1 \\ 0 \\ 0 \\ 2 \\ -1 \\ -1 \\ 0 \\ 0 \end{bmatrix} + D_2 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} + D_3 \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}. \quad (2.7)$$

It includes the orbital splittings of $4d$ orbitals in the tetragonal crystal field. The constant D_1 serves as a crude estimate of the splitting between the orbital xy and the orbital doublet $\{yz, zx\}$, i.e., when taking into account only H_{diag} while neglecting the remaining parts of the full Hamiltonian,. For $D_1 < 0$ (like in Ca_2RuO_4) in the presence of a tetragonal distortion of RuO_6 octahedra the xy orbital has a lower energy and is occupied (in the atomic configuration) by two electrons, while yz and zx are occupied by one electron each — then the energy

gain is D_1 , i.e., such an occupation pattern is more stable. For $D_1 > 0$ (like in Sr_2RuO_4) the doublet $\{yz, zx\}$ has a lower energy and is more stable. The parameters D_2 and D_3 follow from the estimates of the splitting between t_{2g} and e_g orbitals. They do not influence the ground state energy if only t_{2g} orbitals are occupied, while there is a punishment (by the value of D_2 or D_3) for each electron occupying x^2-y^2 or $3z^2-r^2$ level respectively. These parameters $\{D_2, D_3\}$ are much larger than D_1 in the case of Sr_2RuO_4 and the difference between them is rather small.

Jahn-Teller part can be neglected in the Hamiltonian (2.1). The exception is the elongation of bonds between ruthenium and apical oxygens which could be considered as a frozen global (static) Q_3 Jahn-Teller distortion [1] but it is much simpler to include it by a proper renormalization of the crystal-field splittings. Note that in the other compound Ca_2RuO_4 Jahn-Teller effects are large (see for example Ref. [21]) and as a result the symmetry of the corresponding RuO_4 plane is significantly lowered.

D. Local Coulomb interactions

The last part of the multiband $d-p$ Hamiltonian H_{int} stands for strong on-site Coulomb interactions. For the d orbitals at ruthenium sites it includes Hubbard intraorbital repulsion U_d , Hund's exchange $J_{\mu\nu}^d$ and pair hopping also given by $J_{\mu\nu}^d$,

$$\begin{aligned} H_{\text{int}}^d = & U_d \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow} + \frac{1}{2} \sum_{i,\mu \neq \nu} \left(U_d - \frac{5}{2} J_{\mu\nu}^d \right) n_{i,\mu} n_{i,\nu} \\ & - \sum_{i,\mu \neq \nu} J_{\mu\nu}^d \mathbf{s}_{i,\mu} \cdot \mathbf{s}_{i,\nu} + \sum_{i,\mu \neq \nu} J_{\mu\nu}^d d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow}^\dagger d_{i,\nu,\downarrow} d_{i,\nu,\uparrow}. \end{aligned} \quad (2.8)$$

Here $J_{\mu\nu}^d$ is the tensor of Hund's on-site interorbital exchange elements for d orbitals which can be expressed using Racah parameters B and C [34, 35] (see also Table I given by Horsch in Ref. [36]). Note that we sum twice over each pair $\{\mu\nu\}$ of orbitals in Eq. (2.8). Importance of local Coulomb interactions has been recognized in several model studies [37, 38]. In particular, strong correlations which originate from Hund's coupling have been studied [39] and it was also suggested that this coupling supports the triplet superconductivity [40].

The anisotropy between different Hund's exchange elements $\{J_{\mu\nu}^d\}$ may be neglected as long as one may limit oneself to the orbitals of the same symmetry, i.e., either to t_{2g} or to e_g orbitals [9]. For convenience, we rewrite equation (2.8) as follows

$$\begin{aligned} H_{\text{int}}^d = & U_d \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow} + \frac{1}{2} \sum_{i,\mu \neq \nu,\sigma} (U_d - 3J_{\mu\nu}^d) n_{i,\mu,\sigma} n_{i,\nu,\sigma} + \frac{1}{2} \sum_{i,\mu \neq \nu,\sigma} (U_d - 2J_{\mu\nu}^d) n_{i,\mu,\sigma} n_{i,\nu,-\sigma} \\ & - \sum_{i,\mu \neq \nu} J_{\mu\nu}^d d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow}^\dagger d_{i,\nu,\downarrow} d_{i,\nu,\uparrow} + \sum_{i,\mu \neq \nu} J_{\mu\nu}^d d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow}^\dagger d_{i,\nu,\downarrow} d_{i,\nu,\uparrow}. \end{aligned} \quad (2.9)$$

Similarly, local Coulomb interactions at oxygen sites (for $2p$ orbitals) are given by

$$\begin{aligned} H_{\text{int}}^p = & U_p \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow} + \frac{1}{2} \sum_{i,\mu \neq \nu,\sigma} (U_p - 3J_{\text{H}}^p) n_{i,\mu,\sigma} n_{i,\nu,\sigma} + \frac{1}{2} \sum_{i,\mu \neq \nu,\sigma} (U_p - 2J_{\text{H}}^p) n_{i,\mu,\sigma} n_{i,\nu,-\sigma} \\ & - \sum_{i,\mu \neq \nu} J_{\text{H}}^p p_{i,\mu,\uparrow}^\dagger p_{i,\mu,\downarrow}^\dagger p_{i,\nu,\downarrow} p_{i,\nu,\uparrow} + \sum_{i,\mu \neq \nu} J_{\text{H}}^p p_{i,\mu,\uparrow}^\dagger p_{i,\mu,\downarrow}^\dagger p_{i,\nu,\downarrow} p_{i,\nu,\uparrow}, \end{aligned} \quad (2.10)$$

where all off-diagonal elements $J_{\mu\nu}^p$ are equal as they connect the orbitals of the same symmetry, i.e., $J_{\mu\nu}^p \equiv J_H^p$. Up to now this latter part (H_{int}^p) was neglected in the majority of studies, i.e., they assume $U_p = J_H^p = 0$. As a compensation some effective and appropriate modification of the charge-transfer energy has to be performed. Indeed, it has been shown for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ cuprates employing constrained local density approach that the estimation of U_p is very sensitive to the assumed value of Δ [41] — the value of $\Delta = 2.0$ eV yields $U_p \sim 8$ eV, while $\Delta = 4.0$ eV yields $U_p \sim 4$ eV. One notes that there is a roughly linear dependence of U_p on Δ to reproduce a constant value of the charge-transfer gap in Hartree-Fock [42]; at the same time the estimated value of U_d remains more or less constant.

Unfortunately, not much is known about the real value of Δ (2.5) for different compounds. Estimates based on LDA results for Sr_2RuO_4 gave the value $\Delta \sim 1.5$ eV [32]. This value is much lower than $\Delta \sim 8$ eV used in Ref. [33] (where also $U_p = 0$ was assumed). All these estimations come from different fitting procedures employing numerous simplifying assumptions. One has to realize that Δ (2.5) is not an *ab initio* like value in the framework of $d-p$ model but rather some effective value which better should be treated as a free parameter (the $d-p$ model itself is an effective model, and definitely not an *ab initio* model). Thus in the following we will vary the value of Δ from 0 to 6.0 eV. We do not consider negative values of Δ as their consequence are greatly overcharged d -shells. We also remark that it has been realized nowadays that effective models with only d orbitals are insufficient and many papers treat electronic oxygen degrees of freedom explicitly. For cuprates this subject has a long history and realistic $d-p$ models were studied for CuO_3 chains [42, 43] and for CuO_2 planes [4, 44, 45]. The oxygen orbitals are also of importance for ruthenates such as in Sr_2RuO_4 [46] and for other correlated oxides [47–49].

III. SETTING THE HAMILTONIAN PARAMETERS

A. Previous studies of the charge-transfer model

The effective $d-p$ model requires a choice of a number of explicitly included parameters. In the extreme case when only $4d$ orbitals are used in a tight-binding (semiempirical) model [23] the parameters are very different from the cases where Coulomb interactions are treated in the Hartree-Fock approximation. Here we adopt in-plane hopping elements ($pd\sigma$), ($pd\pi$), ($pp\sigma$) and ($pp\pi$) used in [33]: $-3.4, 1.53, 0.6, -0.15$ (all in eV). The out-of-plane hoppings (involving the apical oxygens) were scaled using the formulae from the book by Harrison [50]: $-2.6, 1.167, 0.559, -0.140$ (all in eV). A similar value of ($pd\pi$) = 1.5 eV for the in-plane hopping was reported earlier by Oguchi [31] who applied the tight-binding formulae to fit the LDA electronic structure. Different es-

timations for ($pd\pi$) are quite close to one another; they read as follows: (i) 1.0 eV in Ref. [51]; (ii) ~ 1 eV as used by the group of Fujimori's [30]; (iii) 0.85 eV in Ref. [32]. Let us note that for cuprates frequently accepted values for ($pd\pi$) are 0.75 eV in Ref. [41] and 0.9 eV in Ref. [4].

The choice of the Coulomb elements is rather difficult due to their considerable screening in the oxides which is however less efficient in $4d$ systems [49]. For the intraorbital Coulomb repulsion U_d at ruthenium sites the value of ~ 3 eV is most frequently used [30, 33, 52, 53]. We fix here $U_d = 3.1$ eV following Ref. [52]. We remark that we cannot follow popular estimations made by Okamoto and Millis [54] and by Liebsch [55] as they apply to effective models featuring only Ru sites renormalized by the hybridization with oxygen orbitals.

Hund's exchange elements are less screened than intraorbital Coulomb elements and close to their atomic values (see for example Ref. [56]). For Hund's exchange J_H^d between two t_{2g} electrons various estimates range from 0.5 eV up to 0.8 eV: (i) 0.5 eV in Refs. [33, 53]; (ii) 0.6–0.8 eV in Ref. [57]; (iii) 0.7 eV in Ref. [52]; (iv) 0.8 eV in Ref. [18]. We will use $J_H^d = 0.7$ eV. Moreover, for the sake of fixing precisely Hund's coupling tensor elements $J_{\mu,\nu}^d$ we use Table I from Ref. [36] and in addition we use an empiric formula $C \simeq 4B$ for Racah parameters. With this *Ansatz* for a pure t_{2g} system $J_H^d = 3B + C \approx 7B$ and $B = 0.1$ eV [9]. This determines the $J_{\mu,\nu}^d$ elements when e_g levels are not empty (using again the entries from Table I in Ref. [36]).

For the intraorbital Coulomb repulsion at oxygen sites U_p (in ruthenates) again not much is known and it was neglected in several studies. In Ref. [57] this element is estimated to be $U_p = 4 - 6$ eV. In cuprates the available data are more abundant: U_p is 4.5 eV in Ref. [4], ~ 4 eV in Refs. [41, 58]; while several possibilities were also given (all in the range 3–8 eV) with 6 eV indicated by some experimental data [59]. We use below $U_p = 4.4$ eV. For Hund's coupling at oxygen ions the values $J_H^p = 0.6 - 0.8$ eV were suggested [57], while Grant and McMahan computations in cuprates yield $J_H^p = 0.8$ eV [58]. Following these estimations, we use below $J_H^p = 0.8$ eV. Note that the corresponding tensor $J_{\mu,\nu}^p = J_H^p$ has also the same entries for all off-diagonal elements.

The spin-orbit coupling ζ on Ru sites is usually assumed to be in range from 0.10 to 0.17 eV [8, 29, 30, 33, 60]. Here we follow the most recent experiments which suggest that this coupling is in the middle of this range and take the value $\zeta = 0.13$ eV [8].

To complete the set of the Hamiltonian parameters we have to provide estimates for the crystal-field splittings. The splitting between xy and $\{yz, zx\}$ orbital levels is estimated as: (i) ~ 1 eV in Ref. [32]; (ii) ~ 0.3 eV in Refs. [30, 51]; (iii) 0.1 eV in Ref. [52]. We choose the value 0.1 eV, i.e., we trust the reliable expertise presented in Ref. [52]. The splitting between t_{2g} and e_g orbital levels is 3 eV according to [18] (in Ca_2RuO_4) and up to 3.5 eV [30], while the splitting of 0.8 eV between e_g orbital levels was

TABLE I. Parameters of the Hamiltonian (2.1) (all in eV) used for Hartree-Fock calculations. For the hopping integrals we adopt the values from [33]. Below we present only representative in-plane Slater integrals ($pd\pi$) and ($pp\pi$). Out-of-plane integrals are obtained by applying Harrison scaling. Note that during computations we are setting the value of ε_d to be zero as the reference energy. The value of Δ ($-\varepsilon_p$) is fixed to be the same for in-plane and for apical oxygens and is studied in the range $\Delta \in [0.0, 6.0]$ eV.

U_d	J_H^d	U_p	J_H^p	ζ	D_1	D_2	D_3	$(pd\pi)$	$(pp\pi)$
3.1	0.7	4.4	0.8	0.13	0.10	4.3	3.5	1.53	-0.15

assumed [30]. We accept these values in the parameter set employed in the present calculations (see Table I).

Looking at the parameters, one important remark is proper. Namely the three different values: (i) the absolute value of parameter ($pd\sigma$) which is involved in hopping processes from t_{2g} to e_g orbitals (see Table V in the Appendix); (ii) the value of U_d ; and also (iii) the splitting between t_{2g} and e_g are all close to 3 eV. In other words — the splitting between t_{2g} and e_g does not seem to be large enough to justify the expectation that e_g levels are almost empty.

B. Motivation by earlier *ab initio* results

Let us repeat that in the majority of the papers it is being assumed that e_g levels are entirely empty. However, in the present paper we make an attempt to determine the electron densities in e_g orbitals and to provide a realistic estimate of the charge on oxygens. We remind the reader that we are motivated by the *ab initio* computations performed on a small cluster+embedding by Kaplan and Soullard [24]. We take the liberty to re-

peat, once more, these results as they are really important for a proper understanding of the electronic structure of Sr_2RuO_4 : (i) the p orbital charge on oxygens (in Sr_2RuO_4) is not formal 6.0 but is closer to 5.0 (oxygen s orbitals are also not fully occupied); (ii) the occupation on d orbitals is close to 6 but e_g levels are partly occupied; (iii) charges on strontium ions are not formal 2^+ but rather $\sim 1.6^+$.

Direct mapping of the *ab initio* results to the $d - p$ model is not possible (as the $d - p$ model neglects the valence s orbitals). However, it seems clear that the formal (idealized) ionic model with 6 electrons occupying p levels of each oxygen and 4 electrons occupying d levels of each Ru ion does not apply to the realistic Sr_2RuO_4 . For the sake of convenience let us take a convention and introduce the *self-doping* x for a single RuO_4 unit with respect to the formal idealized model ($x = 0$) while for the real substance we shall consider finite self-doping values such as 1.0, 1.25 and 1.5 ($n = 28 - x$, here we use such simple numbers so as the self-doping translates into integer electron number for the entire cluster).

IV. THE UNRESTRICTED HARTREE-FOCK APPROXIMATION

A. The self-consistent Hartree-Fock problem

We use the unrestricted Hartree-Fock approximation to investigate the model (2.1) for Sr_2RuO_4 . The technical implementation is the same as described in Refs. [26, 33, 53]. Namely, the local Coulomb interaction Hamiltonian H_{intra} is replaced by Hartree-Fock mean-field terms. To give an example, the term according to a common interpretation of Wick, Bloch, and de Dominicis theorem the term $U_d \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow}$ can be replaced (for Hartree-Fock computations) with one-electron operators and double counting correction terms,

$$\begin{aligned} \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow} \simeq & \sum_{i,\mu} \left(\langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\uparrow} \rangle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\downarrow} + d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\uparrow} \langle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\downarrow} \rangle \right) \\ & - \sum_{i,\mu} \left(\langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow} \rangle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\uparrow} + d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow} \langle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\uparrow} \rangle \right) \\ & - \sum_{i,\mu} \left(\langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\uparrow} \rangle \langle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\downarrow} \rangle - \langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow} \rangle \langle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\uparrow} \rangle \right). \end{aligned} \quad (4.1)$$

Note that the terms with superconducting correlations are ignored in the above. Note also that standard mean-field decoupling usually ignores spin-flip terms (second line) [26, 33]. We remind that spin-flip terms do appear in spin-orbit part of the Hamiltonian (2.1), see Eq. (2.3), and have to be included here on equal footing as the mean-field terms.

The averages $\langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\uparrow} \rangle$ and other similar ones can be treated as order parameters. At the beginning some initial values (a guess) have to be assigned to them. During Hartree-Fock iterations the order parameters are recalculated self-consistently until convergence. When decoupling all the terms in H_{int} (2.8) one finds that the

complete set of order parameters is as follows:

$$\begin{aligned} &\langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\uparrow} \rangle, \langle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\downarrow} \rangle, \langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow} \rangle, \langle d_{i,\mu,\downarrow}^\dagger d_{i,\mu,\uparrow} \rangle, \\ &\langle d_{i,\mu,\uparrow}^\dagger d_{i,\nu,\uparrow} \rangle, \langle d_{i,\mu,\downarrow}^\dagger d_{i,\nu,\downarrow} \rangle, \langle d_{i,\mu,\uparrow}^\dagger d_{i,\nu,\downarrow} \rangle, \langle d_{i,\mu,\downarrow}^\dagger d_{i,\nu,\uparrow} \rangle, \end{aligned}$$

where $\mu \neq \nu$. The off-diagonal elements ($\mu \neq \nu$) are of crucial importance, particularly in the present case when finite spin-orbit coupling induces their finite values. A similar set of order parameters has to be considered for the p oxygen orbitals.

B. Hartree-Fock calculations for Sr_2RuO_4

As we mentioned earlier, we are interested only in charge-homogeneous solutions, i.e., homogeneity concerns only primary order parameters ($\mu = \nu$, i.e., charge occupations) but not off-diagonal ($\mu \neq \nu$) order parameters. Thus primary order parameters are translationally invariant according to assumed lattice symmetry. In addition, the symmetry is broken along the z -th axis and the order parameters $\{\langle d_{i,\mu,\uparrow}^\dagger d_{i,\mu,\downarrow} \rangle\}$ are fixed to be zero. Finally, the four-fold symmetry is imposed so that the occupation of p_x and p_y oxygen orbitals is the same, and also of yz and zx orbitals for Ru ions. Altogether we have got 7 independent primary order parameters (per RuO_4 unit) when looking for paramagnetic ground state and 15 for ferromagnetic (or antiferromagnetic) ground states. These numbers are large enough to expect troubles with the Hartree-Fock convergence and indeed this is the case. The regular convergence is found for a very limited set of the Hamiltonian parameters (for example for situations when the oxygen occupations are very close to 6 as was the case in Ref. [33]). A typical situation for our computations is that Hartree-Fock iterations do not converge but oscillate (in a two-cycle) instead.

The standard remedy for poor convergence is the so-called dumping technique, but here it failed, unfortunately. We had to resort to quantum chemistry technique called level shifting [61]. It is based on replacing the Hartree-Fock Hamiltonian by a different Hamiltonian — the one with the identical eigenvectors (one particle eigenfunctions) and with identical occupied eigenenergies. The original eigenenergies of virtual states are all uniformly shifted upwards by a fixed constant value. Thus if we apply the shift say by 1 eV, then the HOMO-LUMO gap (the gap between highest occupied and lowest unoccupied eigenstate) we obtain will be artificially enlarged exactly by 1 eV.

When applying virtual level shifting technique we can obtain valuable information. First case is when the HOMO-LUMO splitting (after correcting for the shift) is negative (for a few different shifts and a few different starting conditions). Then the single-determinant Hartree-Fock ground state we obtain is probably not correct and single-determinant description of the ground

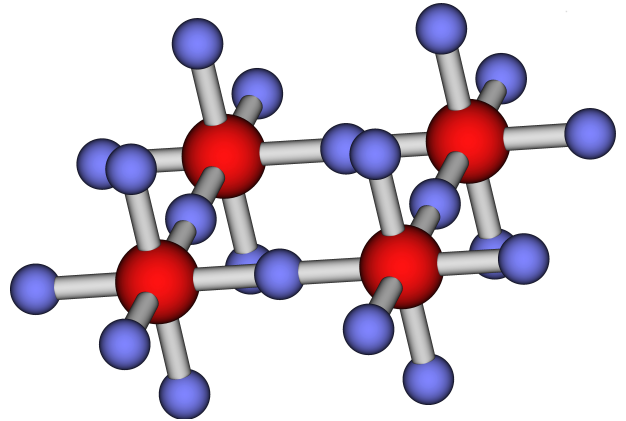


FIG. 1. A fragment of the studied CuO_4 cluster with four Ru ions shown by dark (red) big spheres and surrounding them O ions shown by smaller gray (dark blue) spheres. The calculations in Sec. V were performed for a 4×4 RuO_4 periodic supercell.

state is not possible at all. Multi-configuration Hartree-Fock is required in such a situation instead (and let us remind that the multi-configuration Hartree-Fock still did not mature enough to be a standard working tool in solid state physics). Second case is when HOMO-LUMO gap we obtain is zero (or very close to zero). Then the ground state identification is questionable. However, the probability that such an identification is correct and that the ground state is conducting can be substantial. The probability of correct identification can be further enhanced when performing numerous extra computations: if we obtain the same identification for different shifts and different starting Hartree-Fock conditions, the result is accepted. Finally for the cases with positive HOMO-LUMO gap we usually had no problems.

The computations were performed for a periodic 4×4 RuO_4 supercell with its fragment shown in Fig. 1 (for each particular set of Hamiltonian parameters). They were repeated many times for different starting conditions (different starting charge occupations) and shifts. The state with the lowest Hartree-Fock energy was then identified as the ground state. Numerous runs were necessary as the Hartree-Fock convergence provides many different metastable states (metastable, i.e., only local but not a global minima of the energy). Typical number of runs should be large enough — in some situations more than a hundred. For this very reason the detailed investigation of the phase diagram is too expensive (even for such a small cluster size as we use). Still we performed as many computations for as many different sets of Hamiltonian parameters so as to be sure about the general trends occurring on the phase diagram which are presented in Sec. V.

V. NUMERICAL RESULTS

Numerical studies of the multiband $d-p$ model (2.1) require not only the parameters which were fixed in Sec. III, but also an assumption concerning the total electron number per unit cell. We consider below two different scenarios: (i) the formal ionic model with $n_0 = 4 + 4 \times 6 = 28$ electrons per RuO_4 unit, and (ii) the model with a smaller total number of $n = 28 - x$ electrons, where we investigated a few representative values of *self-doping* $x = 1.0, 1.25, 1.5$. Thereby we concentrate on the most important results obtained for a realistic value of Coulomb interaction within oxygen $2p$ orbitals, $U_p = 4.4$ eV, within the framework of these two different scenarios. As we shall show below, these two situations require quite different values of Coulomb parameter U_p at oxygen $2p$ orbitals.

A. First scenario: Formal ionic model

Taking the ionic model as a starting configuration for the Hartree-Fock iterations, we assume that each oxygen O^{2-} ion has 6 electrons within $2p$ orbitals and each Ru^{4+} ion has 4 electrons within $4d$ orbitals. The RuO_4 unit has a negative charge $Q = 4e$ which is compensated by two Sr^{2+} ions considered only as electron donors to the plane of RuO_4 units. This charge distribution (assumed on start of Hartree-Fock iterations) is however unstable and the electrons quickly redistribute along the iteration process due to $d-p$ hybridization. The final charge distribution is shown in Fig. 2 and in the upper part of Table

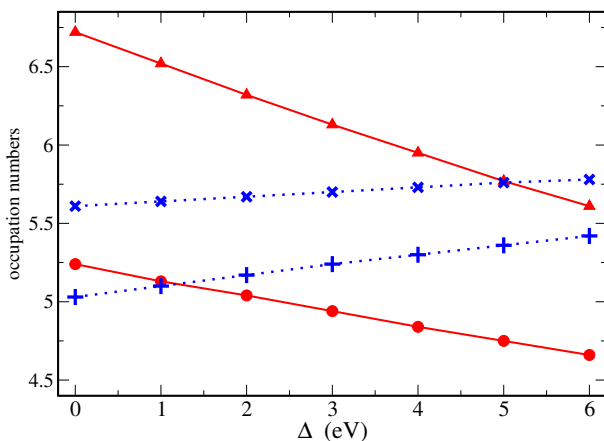


FIG. 2. Electron densities in the multiband model (2.1) for increasing Δ ($\Delta \equiv -\varepsilon_p$) obtained in the formal ionic model (with $n_0 = 28$ electrons per RuO_4 unit): at Ru ions (solid lines) and at O ions (dashed lines). Data points show electron densities within t_{2g} orbitals (n_{t2g} , circles), all $4d$ orbitals (n_{4d} , triangles), $2p$ orbitals at in-plane oxygens ($n_{p\parallel}$, +), and $2p$ orbitals at apical oxygens ($n_{p\perp}$, \times). The obtained ground state is ferromagnetic.

TABLE II. The ground state obtained in the formal ionic model with $n_0 = 28$ ($x = 0$) electrons and in the realistic model with self-doping ($x > 0$): HOMO-LUMO gaps G (eV), the total magnetic moment m_{tot} per RuO_4 unit, and the magnetic moment at Ru ions m_{Ru} obtained for several values of Δ (eV). Note that when the total magnetization m_{tot} is large, it is mainly due to the magnetization at oxygen ions.

x	energies (eV)		magnetizations	
	Δ	G	m_{tot}	m_{Ru}
0.00	0.0	0.10	1.00	0.34
	1.0	0.29	0.75	0.32
	2.0	0.39	0.75	0.36
	3.0	0.43	0.75	0.40
	4.0	0.46	0.75	0.45
1.00	0.0	0.27	1.25	0.30
	1.0	0.10	0.24	0.09
	2.0	0.30	0.24	0.11
	3.0	0.33	0.24	0.12
	4.0	0.35	0.24	0.14
1.25	0.0	~ 0	1.12	0.26
	1.0	~ 0	0.12	0.11
	2.0	0.04	0.11	0.05
	3.0	0.04	0.11	0.06
	4.0	0.04	0.11	0.06
1.50	0.0	0.22	0.20	0.18
	1.0	0.21	0.00	0.00
	2.0	0.26	0.00	0.00
	3.0	0.38	0.00	0.00
	4.0	0.51	0.00	0.00

II. As expected, the total (n_{4d}) and partial (n_{t2g}) electron densities at Ru ions increase with increasing value of ε_p (i.e., decrease with increasing value of Δ) which follows from electron transfer from O to Ru ions.

The ground state (in the entire range of the investigated values of ε_p) is ferromagnetic and insulating, which is surprising and does not agree with *ab initio* calculations [14]. It could be argued that Hund's exchange is strong enough to polarize the $4d$ electrons if t_{2g} orbitals are well away from half filling ($n_{t2g} > 4.7$ for the considered range of ε_p), in spite of large $d-p$ hybridization. The instability towards ferromagnetism competes here with $d-p$ hybridization and therefore the magnetic moment per RuO_4 unit is small. The nonmagnetic ground state is metastable, and has a higher energy by about 0.8 eV (per RuO_4 unit). Also, the occupation patterns for the obtained ground states do not agree with the *ab initio* data [24]. It is well known that Sr_2RuO_4 has a paramagnetic and metallic ground state. Thus, the model (2.1) for the adopted parameter values and within the first scenario is clearly not realistic enough for Sr_2RuO_4 .

B. Second scenario: Realistic self-doping model

In the second scenario we follow the results presented in [24] and we assume a reduced total number of electrons per RuO_4 unit. Taking the total electron number $n = 28 - x$ with $x > 0$ this corresponds to finite hole *self-doping*, and we study here $x = 1.00, 1.25, 1.50$. For the missing electrons the smaller (than in the ideal-ionic-model) transfer of valence $4s$ electrons from Sr sites is mainly responsible ($5s$ valence electrons on Ru, neglected in the $d-p$ model, have also some minor influence). The corresponding electron densities obtained for $x = 1.50$ are shown in Fig. 3 and in Table II.

The difference between the two density distributions shown in Figs. 2 and 3 is mainly visible in the electron densities at Ru ions. At finite self-doping of $x = 1.5$ the total electron density within $4d$ orbitals is close to $n_{4d} = 5$ for a value $\Delta \simeq 5.0$ eV, while it is close to $n_{4d} = 5.5$ for the same value of Δ in the ionic model. The electron density at in-plane oxygens is also somewhat reduced in the former case. These orbitals are influenced stronger by the self-doping as they are hybridized with the t_{2g} orbitals at the central Ru ion in each RuO_4 unit, and provide also bonding between these units.

Our calculations demonstrate that the metallic non-magnetic state observed in Sr_2RuO_4 is realized when the density of electrons within Ru t_{2g} orbitals is not close to half filling, i.e., $n_{t_{2g}} < 4.5$. Such a nonmagnetic state is found in the present realistic model with self-doping when of $2p$ energy $\Delta > 1.0$ eV. On the contrary, when $x \in [1.25, 1.50]$ and $\Delta \in [0.0, 1.0]$ eV, the ground state is

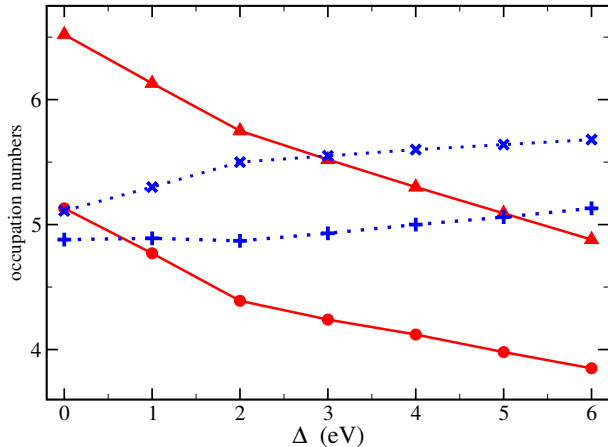


FIG. 3. Total electron densities in the realistic $d-p$ multi-band model based on *ab initio* calculations for increasing Δ ($\Delta = -\varepsilon_p$) for Ru(t_{2g}) orbitals (solid line, circles), Ru($4d$) orbitals (solid line, triangles) and O($2p$) orbitals (dashed lines). There are $(4 \times 6 + 2.5)$ electrons per a single RuO_4 unit, corresponding to self-doping by $x = 1.5$ electrons. The ground state is nonmagnetic for $\Delta > 1.0$ eV, and weakly ferromagnetic for $\Delta \leq 1.0$ eV. The change of magnetic order is responsible for the change of the slope of the lines.

TABLE III. Hartree-Fock energy E_{HF} , the HOMO-LUMO gap G , electron densities within t_{2g} orbitals ($n_{t_{2g}}$), for all $4d$ orbitals (n_{4d}), oxygen $2p$ orbitals at in-plane oxygens ($n_{p\parallel}$), and oxygen $2p$ orbitals at oxygens in apical positions ($n_{p\perp}$), and total magnetic moments m_{tot} (per RuO_4 unit), for a few selected ground states with the total electron number $n = 28 - x$ per RuO_4 unit. Parameter: $\Delta = 1.0$ eV.

x	energies (eV)		electron densities				
	E_{HF}	G	$n_{t_{2g}}$	n_{4d}	$n_{p\parallel}$	$n_{p\perp}$	m_{tot}
1.00	111.049	0.24	4.78	6.19	4.95	5.45	0.10
1.25	107.838	0.12	4.85	6.21	4.95	5.32	0.00
1.50	104.663	0.00	4.77	6.13	4.89	5.30	0.21

ferromagnetic. Metallic ferromagnetism is here possible due to large values of the Stoner parameter $I \simeq U_d + 2J_H^d$ for partly filled t_{2g} orbitals [62] which is farther enhanced by partly occupied e_g orbitals. Effectively I is enhanced here when the density of $4d$ electrons is increased and e_g orbitals are also partly filled as we have seen in the ionic model.

The most interesting data obtained in our Hartree-Fock calculations for the realistic model are presented in Table III. Here we identify the region of phase diagram where both the HOMO-LUMO gap G is small or vanishes and the ground state is close to a transition from a non-magnetic to ferromagnetic one. In this regime one finds large electron density within e_g orbitals accompanied by rather strong reduction of electron density at the oxygen ions in RuO_2 planes. The density at these ions $n_{p\parallel}$ varies from 4.95 to 4.89 when $x \in [1.0, 1.5]$, i.e., each oxygen ion contains one hole and is rather close to the O^{1-} ionic state. These results of our computations agree well enough with the results of Ref. [24]. Indeed, the charge on oxygen ions, in particular the ones lying within RuO_2 planes, is close to 5 and not to formal 6 electrons per ion. This demonstrates the metallic character of the electronic structure in Sr_2RuO_4 . We emphasize that the occupations which follow from the present model are close to those reported in the *ab initio* investigation [24] — some representative examples of the occupations obtained in the Hartree-Fock calculations are shown in Table III (see also Fig. 3).

C. Importance of Coulomb interactions at oxygen ions

We have verified that actual electron densities within $2p$ orbitals are rather sensitive to the used Coulomb interaction parameters at oxygen ions. To obtain unphysical density of $n_{p\parallel} \simeq 6$ at in-plane oxygen ions (as in the formal ionic model) one must require that $U_p = 0$ and/or ε_p must be very large negative, i.e., the charge-transfer gap Δ has to be very large. This is confirmed by all test computations performed varying the values of U_p and ε_p .

Using the set of Hamiltonian parameters from Table

TABLE IV. Hartree-Fock results for ferromagnetic ground states obtained using three different multiband models in absence of electron interactions at oxygen ions ($U_p = J_H^p = 0$): total electron densities within t_{2g} orbitals ($n_{t_{2g}}$), for all $4d$ orbitals (n_{4d}), oxygen $2p$ orbitals at in-plane oxygens ($n_{p\parallel}$), and oxygen $2p$ orbitals at oxygens in apical positions ($n_{p\perp}$), total magnetization m_{tot} per RuO_4 unit, HOMO-LUMO gap G (eV), and spin-orbit contribution per single Ru $\langle H_{so}^{(i)} \rangle$ (eV). In the third segment all HOMO-LUMO gaps G are zero (within 1 meV accuracy), thus the reliable identification of the ferromagnetic ground state is not possible (but probable).

model	x	energies (eV)			electron densities				
		Δ	G	$\langle H_{so}^{(i)} \rangle$	n_{t2g}	n_{eg}	$n_{p }$	$n_{p\perp}$	m_{tot}
I, all $4d$	0.0	0.0	0.39	-0.076	4.19	0.51	5.75	5.91	1.0
		3.0	0.34	-0.083	4.12	0.40	5.81	5.93	1.0
		6.0	0.16	-0.088	4.08	0.31	5.85	5.95	1.0
I, only t_{2g}	0.0	0.0	0.37	-0.043	4.24	-	5.91	5.98	1.0
		3.0	0.35	-0.049	4.14	-	5.94	5.99	1.0
		6.0	0.20	-0.052	4.09	-	5.96	5.99	1.0
realistic	1.5	0.0	~ 0	-0.026	2.90	0.62	5.63	5.86	1.25
		3.0	~ 0	-0.025	2.76	0.50	5.73	5.91	1.25
		6.0	~ 0	-0.025	2.67	0.37	5.80	5.93	1.25

1 but setting $U_p = J_H^p = 0$ (while keeping other parameters unchanged) we performed additional Hartree-Fock computations to investigate importance of Coulomb repulsion at oxygen ions. These calculations gave very different electron density distributions than those obtained before for the same values of Δ and total electron density n , but with finite U_p and J_H^p . As shown in Table IV, one finds large electron densities at in-plane oxygens, $n_{p\parallel} > 5.75$, and only ferromagnetic ground states in the entire range of $\varepsilon_p \in [-6, 0]$. It may be considered quite unexpected that the $2p$ oxygen orbitals are almost completely filled then even at $\varepsilon_p = 0$. The almost ionic state O^{2-} is here a consequence of Coulomb repulsion at Ru ions which blocks electron redistribution due to hybridization. It is also surprising that the same Hartree-Fock energy is obtained for ferromagnetic and for antiferromagnetic ground states. Note that for the pure t_{2g} model (when setting $D_2 \gg 1$ and $D_3 \gg 1$) and for large $\Delta = 6.0$ eV (when t_{2g} occupation number is equal to formal $n_{t_{2g}} = 4$) the nonmagnetic ground state has a higher energy by ~ 0.8 eV than the ferromagnetic one.

VI. DISCUSSION AND SUMMARY

Altogether the results of the presented Hartree-Fock computations are too complex to be fully conclusive, but nevertheless this study uncovers several important facts concerning the modeling of ruthenium oxides by the multiband charge-transfer model. First of all, the $d-p$ model with a minimal basis set consisting of $\{4d, 2p\}$

orbitals is a useful tool for investigating the electronic structure when the effective electron density within the considered basis set is established in agreement with the experimentally observed ground states. We have found that a significant electron charge is transferred *beyond* the $d-p$ orbitals and thus the effective electron density within the RuO_4 units has to be reduced to $n = 28 - x$, with $x \in [1.0, 1.5]$. This effect is similar to the reduction of electron density in $d-p$ orbitals in cuprates, where $4s$ orbitals at Cu ions are also partly occupied [63]. Another reason responsible for this appreciably reduced electron density could be a partial charge transfer from oxygen orbital to the charged Sr ions in Sr_2RuO_4 , suggesting that the ionic picture with Sr^{2+} ions transferring 2 electrons to the RuO_4 subsystem is oversimplified.

We have shown that Coulomb interaction effects at oxygen ions are very important and have to be included in a realistic description of these materials. Only then the hybridization effects are strong enough and are able to overcome Hund's exchange at ruthenium ions which otherwise induces metallic ferromagnetic state, contrary to the experimental observations. We note however that ferromagnetic instability was observed in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ systems where antiferromagnetic interactions are also possible [64]. This is reminiscent of the situation encountered in the $\text{Ca}_{1-x}\text{Sr}_x\text{RuO}_3$ perovskites, with CaRuO_3 found to be on the verge of a ferromagnetic instability [65]. Therefore, we suggest that further research in a model including lattice distortions is required to establish the range of stability of ferromagnetism in the layered $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ systems, being to some extent also expected from the present results.

An extension of this model could be used for a similar modeling of the electronic structure of Ca_2RuO_4 , but this would also require Jahn-Teller coupling to the lattice to describe correctly the lattice distortions which accompany the insulating state. It remains a challenge for the theory to establish whether the electron density within the multiband $d-p$ model would not be increased by such an insulating state and we suggest that the self-doping effect described here would be concentration dependent in the $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ compounds.

In summary, the most important consequence of both $d-p$ hybridization and spin-orbit coupling is the electron transfer from t_{2g} to e_g orbitals as our calculations demonstrate that e_g orbitals at Ru ions are partly occupied in the realistic parameter regime. Thus, e_g orbitals have to be included in any realistic model for ruthenium oxides. This invalidates the paradigm that ruthenium oxides are pure t_{2g} systems. A second very important effect is a significant reduction of the electron density within oxygen orbitals from the values obtained in the ionic model, which effectively corresponds to one hole per oxygen ion within RuO_2 planes. Finally, only when the above self-doping effect is included, the nonmagnetic metallic state of Sr_2RuO_4 may be correctly described.

TABLE V. The non-zero ruthenium-oxygen hopping elements in RuO_4 plane as obtained using Slater-Koster rules [50, 66]. $(pd\pi)$ and $(pd\sigma)$ are the appropriate Slater-Koster interatomic integrals [50, 66]. We assume that oxygen ions belonging to the i^{th} RuO_6 octahedron are reached by in-plane vectors $\pm\mathbf{a}_1 = \pm a(1, 0, 0)$, $\pm\mathbf{a}_2 = \pm a(0, 1, 0)$, and the apical oxygen positions by out-of-plane vectors, $\pm\mathbf{a}_3 = \pm b(0, 0, 1)$. We use standard notation, with $\mathbf{R} = \mathbf{R}_i - \mathbf{R}_j$ being the vector for a nearest neighbor bond between ruthenium at site i and oxygen at site j , while the coordinates (l, m, n) of \mathbf{R}/R which stand for the direction cosines of the hopping.

\mathbf{R}	(l, m, n)	ν	μ	$t_{j,\nu;i,\mu}$
$\pm\mathbf{a}_1$	$(\pm 1, 0, 0)$	x	$x^2 - y^2$	$l(\frac{\sqrt{3}}{2})(pd\sigma)$
	$(\pm 1, 0, 0)$	x	$3z^2 - r^2$	$-l(\frac{1}{2})(pd\sigma)$
	$(\pm 1, 0, 0)$	y	xy	$l(pd\pi)$
	$(\pm 1, 0, 0)$	z	zx	$l(pd\pi)$
$\pm\mathbf{a}_2$	$(0, \pm 1, 0)$	y	$x^2 - y^2$	$-m(\frac{\sqrt{3}}{2})(pd\sigma)$
	$(0, \pm 1, 0)$	y	$3z^2 - r^2$	$-m(\frac{1}{2})(pd\sigma)$
	$(0, \pm 1, 0)$	x	xy	$m(pd\pi)$
	$(0, \pm 1, 0)$	z	yz	$m(pd\pi)$
$\pm\mathbf{a}_3$	$(0, 0, \pm 1)$	z	$3z^2 - r^2$	$n(pd\sigma)$
	$(0, 0, \pm 1)$	x	xz	$n(pd\pi)$
	$(0, 0, \pm 1)$	y	yz	$n(pd\pi)$

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APPENDIX

The non-zero ruthenium-oxygen $d - p$ and oxygen-oxygen $p - p$ hopping elements obtained by using Slater-Koster rules [66] for the lattice constant $a = 1$ are presented in Tables V and VI, respectively.

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TABLE VI. The non-zero oxygen-oxygen hopping elements in RuO_4 plane as obtained using Slater-Koster rules [50, 66]. $(pp\pi)$ and $(pp\sigma)$ are the appropriate Slater-Koster interatomic integrals [50, 66]. We use a standard notation as explained in Table V, with symbols (l, m, n) standing for the direction cosines of the hopping.

$p - p$ hopping	(l, m, n)	ν	μ	$t_{j,\nu;i,\mu}$
$2p_{\parallel} - 2p_{\parallel}$	$(\pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2}, 0)$	x	x	$(\frac{1}{2})[(pp\sigma) + (pp\pi)]$
	$(\pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2}, 0)$	y	y	$(\frac{1}{2})[(pp\sigma) + (pp\pi)]$
	$(\pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2}, 0)$	z	z	$(pp\pi)$
	$(\pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2}, 0)$	x	y	$lm[(pp\sigma) - (pp\pi)]$
$2p_{\parallel} - 2p_{\perp}$	$(\pm\frac{\sqrt{2}}{2}, 0, \pm\frac{\sqrt{2}}{2})$	x	x	$(\frac{1}{2})[(pp\sigma) + (pp\pi)]$
	$(\pm\frac{\sqrt{2}}{2}, 0, \pm\frac{\sqrt{2}}{2})$	y	y	$(pp\pi)$
	$(\pm\frac{\sqrt{2}}{2}, 0, \pm\frac{\sqrt{2}}{2})$	z	z	$(\frac{1}{2})[(pp\sigma) + (pp\pi)]$
	$(\pm\frac{\sqrt{2}}{2}, 0, \pm\frac{\sqrt{2}}{2})$	x	z	$ln[(pp\sigma) - (pp\pi)]$
$2p_{\parallel} - 2p_{\perp}$	$(0, \pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2})$	x	x	$(pp\pi)$
	$(0, \pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2})$	y	y	$(\frac{1}{2})[(pp\sigma) + (pp\pi)]$
	$(0, \pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2})$	y	z	$mn[(pp\sigma) - (pp\pi)]$
	$(0, \pm\frac{\sqrt{2}}{2}, \pm\frac{\sqrt{2}}{2})$	z	z	$(\frac{1}{2})[(pp\sigma) + (pp\pi)]$

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